



Emerging hollow artificial photosynthetic system with S-scheme heterojunction sandwiched between layered redox cocatalysts for overall CO₂ reduction and H₂O oxidation

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ABSTRACT

The development of artificial photosynthesis is challenged by nonstoichiometric photocatalytic reaction of CO₂ with H₂O. Herein, a delicate hollow multi-shelled nanoreactor with S-scheme heterojunction sandwiched between layered noble-metal-free redox cocatalysts is fabricated, which exhibits excellent photocatalytic performance for overall CO₂-to-CO reduction and H₂O-to-O₂ oxidation with stoichiometric ratio of the evolved reduction and oxidation products. The synergy of the sandwiched heterojunction and spatially separated dual cocatalysts on the inner/outer sides: (i) promotes the separation and transfer of powerful photoexcited charges towards opposite directions; (ii) maneuvers the occurrence of surface redox reactions in different spaces through lowering the thermodynamic barriers, and (iii) hinders the occurrence of side reactions and photocorrosion on the semiconductor surface. Consequently, the charge separation, transfer and consumption are well balanced, and the photocatalytic activity, selectivity and stability are perfectly optimized. It is expected that this novel design can be extended to other semiconductor heterojunctions towards high-efficient photoredox catalysis.

1. Introduction

Mimicking natural photosynthesis to convert CO₂ with H₂O into value-added chemicals or fuels via solar energy holds promise to close the carbon cycle and fulfill the energy demand [1–4]. Unfortunately, its practical application is restricted by low solar-to-chemical energy conversion efficiency because of insufficient light utilization, rapid electron-hole recombination, sluggish catalytic reactivity, and undesirable side/reverse reactions in most of established semiconductor photocatalysts [5,6]. Particularly, it is difficult for a single-component semiconductor photocatalyst to simultaneously possess wide optical absorption range and strong redox capabilities. Besides, some photocatalysts only work in the presence of a hole scavenger resulted from mismatched energy band structure [7,8], while others exhibit

incompatible O₂ evolution much lower than stoichiometric ratio owing to unbalanced transfer and consumption of photogenerated electrons and holes [9,10]. Generally, the mobility of holes is significantly lower than that of electrons [11]. Meanwhile, four-electron-proton coupled oxygen evolution reaction is a slow kinetics process requiring relatively high energy to overcome the barrier, thus becoming the bottleneck of overall redox reactions [12]. Therefore, it is highly desirable to develop elaborated artificial photosynthetic systems not only allowing highly active and selective photoreduction of CO₂ to target product, but also enabling perfect cooperation of CO₂ reduction and H₂O oxidation.

Step-scheme (S-scheme) heterojunction, a rising star in photocatalysis, has demonstrated its multiple advantages to achieve overall redox reactions, which not only settles the trade-off between light absorption and redox potentials of mono-component semiconductor, but

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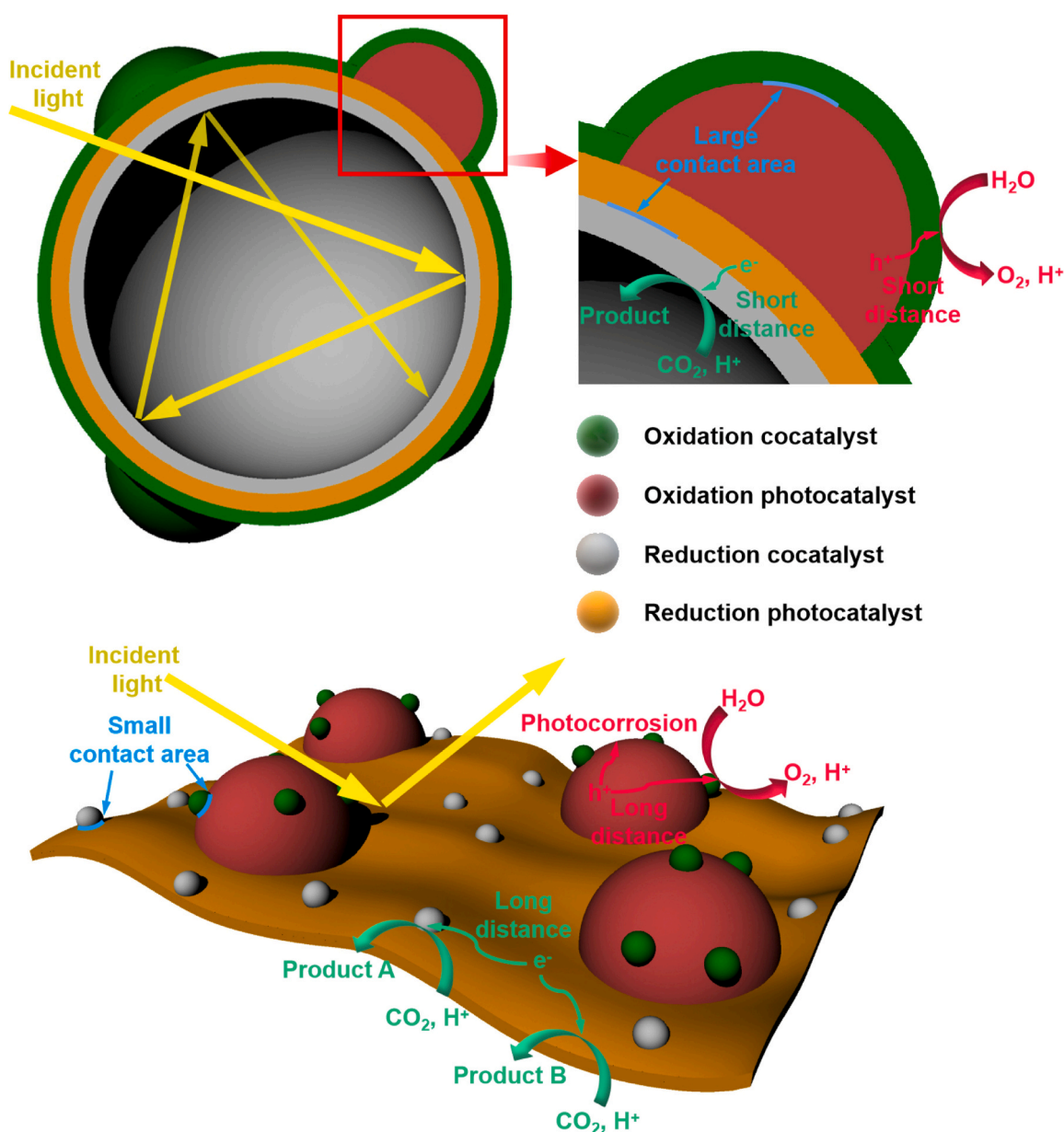
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also balances the separation and transfer of photocarriers [13,14]. A typical S-scheme heterojunction is comprised of a reduction photocatalyst (RP) and an oxidation photocatalyst (OP) with narrow band gap (E_g) and staggered band alignment. With the photoexcitation of RP and OP, weak OP electrons transmit cross the interface and recombine with RP holes, thus separating powerful RP electrons and OP holes for redox reactions. Enabled by the S-scheme heterojunction design, there have been considerable photoactivity enhancements in CO_2 reduction and other applications [15–17]. Nevertheless, existing S-scheme heterojunctions still suffer from unsatisfactory CO_2 conversion efficiencies, poor product selectivities, and mismatched O_2 evolution, since the lack of robust and well-defined redox sites on the semiconductor surface modulating the reaction kinetics, regulating the CO_2 reduction pathways, and balancing the electron-hole consumption [18].

Introduction of proper cocatalysts represents an effective strategy to overcome above obstacles and optimize the catalytic reactivities of S-scheme heterojunctions [19–21]. Reduction and oxidation cocatalysts respectively trap photoelectrons and holes from light-harvesting

semiconductors and provide highly active sites for redox reactions. However, a simple implantation of dual cocatalysts with a random distribution only gives rise to more serious carrier recombination and severe back reactions [22,23]. It is of utmost importance to anchor reduction and oxidation cocatalysts separately on the RP and OP surface of an S-scheme heterojunction [24]. Selective photodeposition of noble metal (e.g. Pt, Pd and Au) and their derivatives (e.g. IrO_2 and RuO_2) may be a potential method, which however is unsustainable and economically unsound due to scarcity and high cost of precious metal [25,26]. Furthermore, the vast majority of reported cocatalysts are discrete on the semiconductor surface. As illustrated in Scheme 1, the small contact area between light-harvesting semiconductor and cocatalyst cannot provide sufficient channel for interfacial charge transfer, and the long carrier-migration distance from the former to the latter inevitably increases the probability of charge recombination loss. Resulted from the sluggish charge transfer, part of active charges move to cocatalyst while others retain on the exposed semiconductor surface for redox reactions. The diverse active sites of cocatalyst and semiconductor cause different



Scheme 1. Schematic illustrating the advantages of sandwiching S-scheme heterojunction between layered redox cocatalysts to construct a hollow artificial photosynthetic system over decorating S-scheme heterojunction with discrete redox cocatalysts.

reaction paths, lowering the product selectivity [27]. Meanwhile, the unconsumed carriers on the semiconductor surface may also induce photocorrosion, attenuating the stability of photocatalyst [28,29]. Therefore, constructing novel artificial photosynthetic systems for better coupling of S-scheme heterojunction and noble-metal-free redox cocatalysts is crucial to take full utilization of their advantages and realize overall conversion of CO₂ with H₂O in high activity, selectivity and stability.

Recently, two-dimensional (2D) layered materials, such as carbonenes (graphene, graphdiyne) [30,31], phosphorenes (black phosphorus) [32], MXene (Ti₃C₂T_x) [33], transition metal dichalcogenides (MoS₂, WS₂) and hydroxides (Ni(OH)₂, Co(OH)₂) [34–37] have emerged as effective noble-metal-free redox cocatalysts in photocatalysis. Different from particulate cocatalysts, as depicted in Scheme 1, 2D structure of cocatalysts allow their face-to-face contact with semiconductors, broadening the space for interfacial charge transfer and shortening the distance for carrier travelling from the latter to the former. Furthermore, the coating of layered cocatalysts can prevent encapsulated semiconductors from participating in side reactions and protect them from photocorrosion. On the other sides, hollow semiconductor nanostructure has shown intrinsic merits in photocatalysis: (i) reinforces the photon absorption via multiple light reflection and scattering in the inner cavities; (ii) provides an ideal platform for the spatial separation of redox cocatalysts inside/outside of the nano-/microreactors [38,39]. Bearing the above points in mind, herein, a hollow artificial photosynthetic system with S-scheme heterojunction (ZnIn₂S₄/Fe₂O₃) sandwiched between layered reduction (carbon) and oxidation (Ni(OH)₂) cocatalysts has been constructed for significantly enhanced photocatalytic performance in overall CO₂ reduction coupled with H₂O oxidation. In the as-synthesized C@ZnIn₂S₄/Fe₂O₃@Ni(OH)₂ photo-reactor (labeled as CZFN), the hollow carbon supporter and Ni(OH)₂ outer layer: (i) drive the flow of electrons and holes with higher redox capacities in opposite directions, maximizing the charge separation efficiency and balancing the consumption of them; (ii) separate the reduction and oxidation half reactions inside and outside the reactor, restraining the occurrence of backward reaction; (iii) improve the adsorption and activation of reactants, lowering the rate-limiting barriers for CO₂-to-CO and H₂O-to-O₂ transformation. As a result, the artificial system exhibits superb activity and selectivity in CO evolution with an apparent quantum efficiency (AQE) of 1.98% at 420 nm. Additionally, the yields of reduction and oxidation products meet almost stoichiometric ratio. To the best of our knowledge, such a hollow photosynthetic system design with Janus layered dual cocatalysts on the two sides of an S-scheme heterojunction has rarely been reported before.

2. Experimental section

2.1. Synthesis of C@ZnIn₂S₄ and ZnIn₂S₄

In a typical synthesis, 3 mL of glycerol and 20 mL of H₂O were injected into a 50 mL round bottom flask, the pH of the solution was adjusted to 2.5 by HCl (0.5 M), which was ultrasonicated for 3 min to obtain a uniform solution. Subsequently, ZnCl₂ (27.2 mg, 0.2 mmol), InCl₃·4 H₂O (58.6 mg, 0.2 mmol) and thioacetamide (30 mg, 0.4 mmol) were added to the above suspension and stirred for 30 min, which is followed by the addition of hollow carbon spheres (2 mg). The resulting mixture was stirred for 10 min and then heated at 80 °C for 2 h. After naturally cooling down to room temperature, the product was collected by centrifuging, washed with ethanol and water thoroughly, and dried at 45 °C in a vacuum. Pristine ZnIn₂S₄ nanosheets were prepared under the same experimental conditions as C@ZnIn₂S₄ except the absence of hollow carbon spheres.

2.2. Synthesis of Fe₂O₃ and C@ZnIn₂S₄/Fe₂O₃

In a typical synthesis of Fe₂O₃ nanocubes, Fe(NO₃)₃·9 H₂O

(64.5 mg, 0.16 mmol) was dissolved in 40 mL of dimethylformamide to form a clear solution after stirring for 5 min at room temperature. The solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave, which was then heated at 180 °C for 6 h. After cooling down to room temperature, the resultant product is washed three times with water and ethanol to remove possible remaining cations and anions, and dried at 45 °C in a vacuum. As for the synthesis of C@ZnIn₂S₄/Fe₂O₃, C@ZnIn₂S₄ and Fe₂O₃ were re-dispersed in water to form 5 and 3 mg mL⁻¹ aqueous suspension, respectively. Subsequently, 1 mL of Fe₂O₃ suspension was dropwise added into 1 mL of C@ZnIn₂S₄ suspension, which is followed by the ultrasonic treatment of the mixed suspension for 5 min. The resultant product was separated by centrifugation, washed with water three times, and dried at 45 °C in a vacuum.

2.3. Synthesis of CZFN and Ni(OH)₂

Ni(NO₃)₂·6 H₂O (72.8 mg, 0.25 mmol) and 50 mL of H₂O were injected into a 100 mL round bottom flask. Subsequently, C₆H₅O₇Na₃ (6.5 mg, 0.025 mmol), hexamethylenetetramine (35 mg, 0.25 mmol), and 40 mg of C@ZnIn₂S₄/Fe₂O₃ were added to above suspension and stirred for 30 min. The resulting mixture was stirred for 10 min and then heated at 90 °C for 10 h. After naturally cooling down to room temperature, the product was collected by centrifuging, washed with ethanol and water thoroughly, and dried at 45 °C in a vacuum. Pristine Ni(OH)₂ nanosheets were prepared under the same experimental conditions as CZFN except the absence of C@ZnIn₂S₄/Fe₂O₃ precursor.

2.4. Synthesis of binary, ternary, and quaternary counterparts

C/Fe₂O₃ and ZnIn₂S₄/Fe₂O₃ were synthesized under the equivalent reaction conditions as C@ZnIn₂S₄/Fe₂O₃ except the use of pure hollow carbon, ZnIn₂S₄ instead of C@ZnIn₂S₄ as a precursor, respectively. ZnIn₂S₄@Ni(OH)₂, Fe₂O₃@Ni(OH)₂, C@ZnIn₂S₄@Ni(OH)₂, C/Fe₂O₃@Ni(OH)₂, and ZnIn₂S₄/Fe₂O₃@Ni(OH)₂ were prepared by following the same procedure as CZFN except the use of ZnIn₂S₄, Fe₂O₃, C@ZnIn₂S₄, C/Fe₂O₃, and ZnIn₂S₄/Fe₂O₃ instead of C@ZnIn₂S₄/Fe₂O₃ as a precursor. C/Fe₂O₃@ZnIn₂S₄ was synthesized under the same experimental conditions as C@ZnIn₂S₄ except the use of C/Fe₂O₃ instead of hollow carbon spheres as a precursor. As for the synthesis of C/Fe₂O₃@ZnIn₂S₄@Ni(OH)₂, C/Fe₂O₃@ZnIn₂S₄ was first prepared according to the synthetic procedure of C@ZnIn₂S₄ except the use of C/Fe₂O₃ instead of hollow carbon spheres as a precursor, which is followed by the coating of Ni(OH)₂ outer layer according to the synthetic procedure of CZFN except the use of C/Fe₂O₃@ZnIn₂S₄ instead of C@ZnIn₂S₄/Fe₂O₃ as a precursor.

2.5. Photocatalytic CO₂ reduction measurements

To investigate the photocatalytic performance of the samples in CO₂ reduction, 20 mg of photocatalyst was dispersed in 2 mL water, and was dispersed on a flat glass plate at the bottom of a 150 mL photocatalytic reactor (Beijing Perfectlight, China). Prior to the test, the reactor loaded with the catalyst was first purged with high purity CO₂ for 15 min in the dark. Then the light-irradiation experiment was performed by using a 300 W Xe lamp (PLS-SXE300D/300DUV, Beijing Perfectlight, China) with visible light as the illumination source, which was realized using both a 420-nm cutoff filter (long-wave-pass) and a 780-nm cutoff filter (short-wave-pass). The power density of visible light (420 < λ < 780 nm) was measured to be 100 mW cm⁻² using a radiometer (FZ-A, China). The photocatalytic reaction was conducted for 4 h under stirring at a rate of 500 rpm. The gaseous mixture was analyzed using a gas chromatograph (GC-2014, Shimadzu) with Ar as the carrier gas. The amounts of H₂ and O₂ were determined using a thermal conductivity detector (TCD). CO was converted to CH₄ by using a methanation reactor and then analyzed using the flame ionization detector (FID). During the stability test, the photocatalyst was collected after each run

and then reused for the photocatalytic reaction. Isotope-labeling experiments were performed using $^{13}\text{CO}_2$ instead of $^{12}\text{CO}_2$, and the products were analyzed using gas chromatography-mass spectrometry (7890B/5977 A, Agilent). The product selectivity was calculated according to the average evolution rates of the reduction products as well as the electrons required to generate products using the following equation:

$$\text{CO selectivity} = 2 \nu(\text{CO}) / [2 \nu(\text{CO}) + 2 \nu(\text{H}_2)] \times 100\% \quad (1)$$

2.6. Apparent quantum efficiency (AQE) measurements

AQE was measured in an identical photosynthesis process except the 420 nm monochromatic incident light provided by a light-emitting diodes (LEDs). AQE is defined as the ratio of the photocatalytic electron consumption (N_{electron}) to the photons flux per hour (N_{photon}), which is calculated according to the formula:

$$\text{AQE}(\%) = N_{\text{electron}} / N_{\text{photon}} = 2 N(\text{CO}) / [(I \times A \times t) / (E_{\text{photon}} \times N_A)] \quad (2)$$

where $N(\text{CO})$ represents the amount of CO; I is the incident light intensity; A is the illumination area which is controlled to 0.82 cm^2 ; t is the illumination time; N_A is Avogadro's constant; and E_{photon} is the average single photon energy, which is figured out using the equation:

$$E_{\text{photon}} = hc/\lambda \quad (3)$$

where h is the Planck constant, c is the speed of light, and λ is the wavelength.

2.7. Electrochemical and photoelectrochemical measurements

5.0 mg of as-prepared samples was uniformly mixed with 30 μL of ethanol, which were then uniformly coated onto a $1 \text{ cm} \times 1 \text{ cm}$ indium tin oxide (ITO) glass. Subsequently, the coated ITO glass was dried at 50°C for 6 h in vacuum. The electrochemical and photoelectrochemical measurements were performed on a CHI 760E electrochemical station (Shanghai Chenhua, China). A standard three electrode system was used consisting of the ITO glass as work electrode, an Ag/AgCl electrode as reference electrode, and a Pt foil as counter electrode, which were inserted in a quartz cell containing 0.5 M Na_2SO_4 solution electrolyte. The electrochemical impedance spectroscopy (EIS) was performed in the 10^{-1} to 10^5 Hz frequency range with an AC voltage amplitude of 10 mV at an applied potential of 0.1 V vs. Ag/AgCl. Photoelectrochemical tests were performed in ambient conditions under irradiation of a 300 W Xe lamp (PLS-SXE300D/300DUV, Beijing Perfectlight, China). The power density of the visible light ($420 < \lambda < 780 \text{ nm}$) was measured to be 100 mW cm^{-2} . The photocurrent density vs. time (I - t) curves of the prepared photoelectrodes was operated at an applied potential of 0.4 V vs. Ag/AgCl under chopped light irradiation (light on/off cycles: 30 s) for 600 s. Transient open-circuit voltage decay (OCVD) measurements were taken for a total of 800 s, and the visible light was switched on and off after 100 and 400 s from the start, respectively. The average lifetimes of the photogenerated carriers (τ_n) were then estimated from the open-circuit voltage (V_{oc}) decay according to the following Equation:

$$\tau_n = -\frac{k_B T}{q} \left(\frac{dV_{\text{oc}}}{dt} \right)^{-1} \quad (4)$$

where τ_n represents the average lifetime, V_{oc} is open-circuit voltage, k_B is the Boltzmann constant, T is the temperature (in Kelvin), and q is the unsigned charge of an electron. Linear sweep voltammetry (LSV) for electrochemical CO_2 reduction was carried out in an Ar-saturated and CO_2 -saturated 0.5 M KHCO_3 solution ($\text{pH} = 7.3$) with a scan rate of 10 mV s^{-1} , respectively. The working electrode was the glassy carbon electrode instead of ITO glass. For electrochemical O_2 evolution

reaction, linear sweep voltammetry (LSV) was carried out in 0.5 M KOH solution (40 mL, $\text{pH} = 13.69$) with a scan rate of 10 mV s^{-1} . The potentials against the Ag/AgCl reference electrode were converted to the RHE reference scale based on the following equation:

$$E(\text{vs-RHE}) = E(\text{vs-Ag/AgCl}) + 0.21 \text{ V} + 0.0591 \times \text{pH} \quad (5)$$

2.8. Sample characterizations

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning TEM (STEM) and energy-dispersive spectroscopy (EDS) mapping profiles were taken on a JEOL JEM-2100 F field-emission high-resolution transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) characterization was carried out on a Zeiss Gemini 300 scanning electron micro-analyzer with an accelerating voltage of 3 kV. Powder X-ray powder diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer with Non-monochromated Cu-K α X-Ray. X-ray photoelectron spectroscopy (XPS) was collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-K α X-ray as the excitation source. In situ irradiated XPS measurements with external visible light source irradiation ($420 < \lambda < 780 \text{ nm}$, PLS-SXE300D/300DUV, Beijing Perfectlight, China) were performed on the basis of XPS measurements. Brunauer-Emmett-Teller (BET) specific surface areas and N_2 adsorption were measured by using a Quantachrome autosorb iQ analyzer at 77 K. CO_2 adsorption was tested using the Quantachrome autosorb iQ analyzer at 298 K. Stead-state photoluminescence (PL) emission spectra were examined using a photoluminescence spectrometer (FLS980, Edinburgh Instruments Ltd.) with a 370-nm excitation wavelength. Raman measurement was carried out on a Renishaw inVia Reflex Raman spectroscope under excitation wavelength of 532 nm. UV-vis diffuse reflectance data were recorded in the spectral region of 200–800 nm with a Cary-7000 series UV-vis-NIR spectrophotometer. Tauc plots were derived from the UV-vis diffuse reflectance spectra according to the equation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (6)$$

where α , $h\nu$ and E_g are the absorption coefficient, photon energy and optical bandgap, respectively. The signal of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ was examined by electron paramagnetic resonance (EPR) spectrometer (Bruker EPR EMXplus) at 9.843 GHz in darkness and under visible light irradiation, respectively. In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was conducted on a Nicolet iN10 Fourier transform infrared spectrometer. The $\text{CO}_2/\text{H}_2\text{O}$ gas was introduced into the sample cell and maintained in darkness for 20 min, and then irradiated by visible light for 70 min

3. Results and discussion

3.1. Sample synthesis and characterization

The synthetic procedure of CZFN is illustrated in Fig. 1a, which starts with the preparation of hollow carbon nanospheres with SiO_2 spheres as templates (step i and ii): monodispersed SiO_2 spheres were firstly synthesized (Fig. S1a,b), followed by the modification and carbonization of polymer layer on the SiO_2 surface (Fig. S1c,d), and finally the removal of the silica core to gain the hollow carbon (Fig. S1e,f) [40]. Scanning electron microscopy (SEM) image in Fig. 1b demonstrates the well-defined hollow carbon spheres with an average diameter of 403 nm, and the mesopore channels in the carbon shell can be seen clearly from TEM image (Fig. 1b and Fig. S2a). Afterwards, ZnIn_2S_4 was in situ grown on the outer surface of carbon spheres to form a hollow C@ ZnIn_2S_4 core-shell structure (step iii). As revealed by SEM and TEM imaging, the exterior surface of carbon spheres is fully covered by

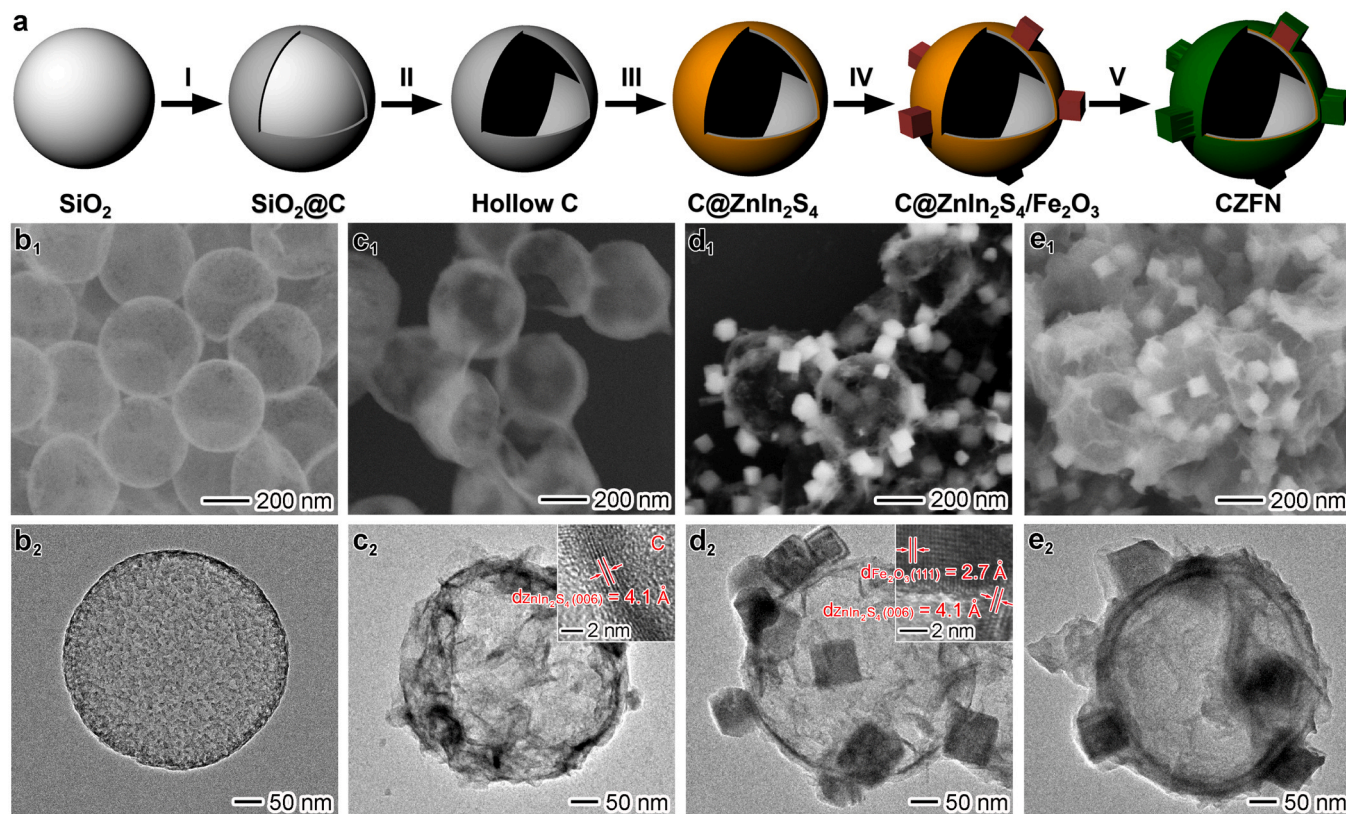


Fig. 1. Formation process of CZFN: (a) schematic illustrating the synthetic process of CZFN; (b-e) SEM and TEM images of (b) hollow C, (c) C@ZnIn₂S₄, (d) C@ZnIn₂S₄/Fe₂O₃ and (e) CZFN.

wrinkled nanosheets with a lattice fringe spacing of 4.1 Å, corresponding to (006) crystal plane of hexagonal ZnIn₂S₄ (Fig. 1c). In the next step, cubic Fe₂O₃ nanocrystals were pre-synthesized (Fig. S3) [41] and deposited on the outer surface of C@ZnIn₂S₄ to obtain C@ZnIn₂S₄/Fe₂O₃ (step iv). SEM and TEM observation reveals that the single-crystalline Fe₂O₃ nanocubes with an average edge length of 69.3 nm are uniformly anchored on the surface of ZnIn₂S₄ supported by carbon spheres (Fig. 1d and Fig. S2b). Finally, the outer surface of C@ZnIn₂S₄/Fe₂O₃ was coated with Ni(OH)₂ nanosheets to fabricate final CZFN (step v). The ultrathin Ni(OH)₂ layer coating on the surface of ZnIn₂S₄ and Fe₂O₃ can be clearly seen from SEM/TEM images in Fig. 1e. Besides, some Ni(OH)₂ nanosheets are also observed to bridge neighboring C@ZnIn₂S₄/Fe₂O₃ to form interlaced networks (Fig. 2a,b). In view of the intimate contact between one face of Fe₂O₃ nanocube with ZnIn₂S₄, Ni(OH)₂ outer layer only covers other five Fe₂O₃ faces, forming a core-shell structure with Fe₂O₃ core enclosed by ZnIn₂S₄ interlayer and Ni(OH)₂ shell (Fig. 2c). In the selected area of the core-shell structure in Fig. 2c, HRTEM image shows clear lattice fringes with spacing of 2.7 and 2.1 Å, corresponding to (111) plane of α -phase Fe₂O₃ and (200) plane of cubic NiO, respectively (Fig. 2d). Since α -Ni(OH)₂ can be easily transformed to NiO under electron beam irradiation, only HRTEM image of evolved NiO can be captured [42]. Further STEM image and the corresponding EDS mapping profiles visualize the elemental distribution of C, Zn, In, S, Fe, Ni and O in the CZFN, validating that the quaternary sample is composed of hollow carbon supporter, ZnIn₂S₄ interlayer, Fe₂O₃ core and Ni(OH)₂ outer shell (Fig. 2e). Apart from CZFN, bare ZnIn₂S₄ and Ni(OH)₂ were also prepared by following the step iii and v synthetic process except the absence of hollow carbon and C@ZnIn₂S₄/Fe₂O₃ precursor, respectively, both of which display flower-like hierarchical microspheres consisting of interweaving nanosheets (Fig. S4 and S5).

Spectroscopic characterizations of CZFN were performed by a combination of XRD, Raman spectroscopy, N₂ sorption isotherm, UV–vis diffuse reflectance spectroscopy and XPS with bare hollow C, ZnIn₂S₄,

Fe₂O₃ and Ni(OH)₂ as reference samples. As depicted in Fig. 2f, all the diffraction peaks in the XRD patterns of ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ match well with the standard card of hexagonal ZnIn₂S₄ (JCPDS-65–2023), rhombohedral hematite (JCPDS-33–0664), and hexagonal Ni(OH)₂ (JCPDS-38–0715), respectively, while no distinct peak can be observed in the pattern of hollow C. The characteristic ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ peaks can be simultaneously observed in the pattern of CZFN. Similar to XRD, Raman spectrum of CZFN exhibits typical peaks including well-documented D and G bands of hollow C, longitudinal optical modes (LO₁ and LO₂) and transverse optical modes (TO₂) of ZnIn₂S₄, A_{1g} and E_g modes of Fe₂O₃, and Ni–O stretching vibration of Ni(OH)₂ (Fig. 2g) [43–45]. According to N₂ adsorption-desorption measurement, BET surface area of hollow C, ZnIn₂S₄, Fe₂O₃, Ni(OH)₂ and CZFN is determined to be 380.1, 18.7, 4.2, 6.6 and 58.2 m² g^{−1}, respectively, reflecting the critical function of hollow porous carbon in boosting the exposed area of CZFN for mass transport (Fig. 2h). Three possible reasons account for the obviously smaller BET surface area of CZFN relative to that of hollow C: (i) ZnIn₂S₄ coverage, Fe₂O₃ loading and Ni(OH)₂ coating, to some extent, block the pores of hollow C and prevent the mass transportation; (ii) a small amount of hollow C might have been damaged during the synthesis of CZFN; (iii) the mass contribution of ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ gives rise to the decrease in the BET area of CZFN [46]. As revealed by UV–vis diffuse reflectance spectra in Fig. 2i, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ exhibit intrinsic bandgap absorption with absorption edge at ca. 470, 600 and 310 nm, respectively, while carbon spheres show broad optical absorption in UV–vis region but without a absorption edge, mainly owing to multiple light reflection and scattering inside the hollow chamber of the zero-bandgap material [47]. As for CZFN, the absorption spectrum is a simple superposition of those of the components involved.

The chemical states of the samples were investigated by XPS. Survey spectrum of CZFN mainly contains the peaks of C1s, Zn2p, In3d, S2p, Fe2p, Ni2p and O1s, in line with the elemental mapping analysis

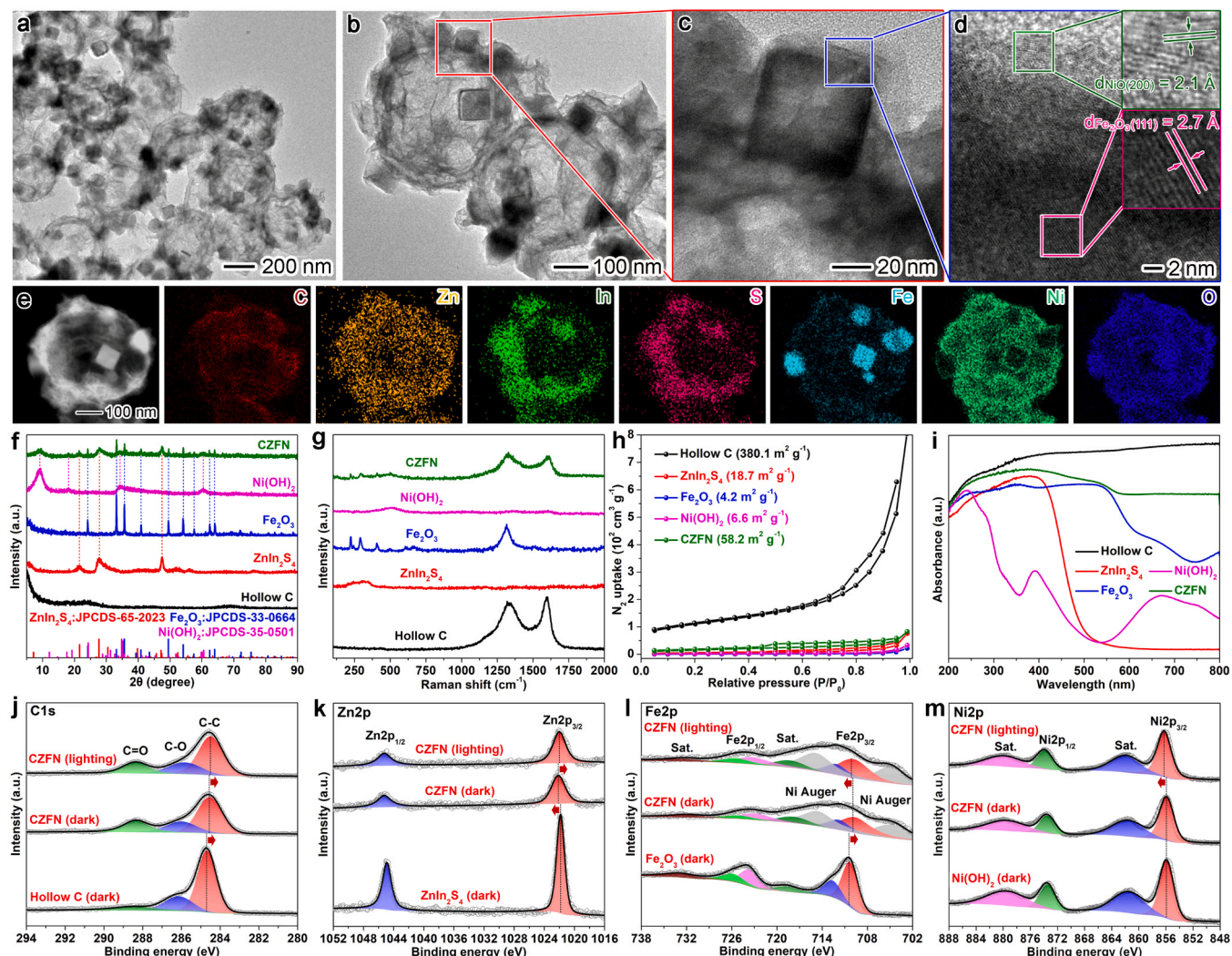


Fig. 2. Detailed characterizations of CZFN: (a-d) TEM and HRTEM images; (e) STEM image and corresponding EDS-mapping profiles; (f-m) spectroscopic characterizations of CZFN with hollow C, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ as reference samples: (f) XRD patterns, (g) Raman spectra, (h) N₂ sorption isotherms, (i) UV-vis diffuse reflectance spectra, (j-m) high-resolution XPS spectra: (j) C1s, (k) Zn2p, (l) Fe2p and (m) Ni2p.

(Fig. S6a). The high-resolution C1s spectra can be deconvoluted to three peaks assigned to C-C, C-O and C=O of hollow C, respectively, and the corresponding binding energies shift to lower values when hollow C is comprised in the CZFN, inferring that carbon supporter acts as an electron-accumulating component (Fig. 2j). Similar phenomenon can be observed in the Zn2p spectrum, in which Zn2p_{3/2} and Zn2p_{1/2} binding energies of CZFN positively shift by 0.32 eV when compared with those of pristine ZnIn₂S₄, disclosing that ZnIn₂S₄ becomes electron deficient upon the formation of the hybrid (Fig. 2k). The electron-deficient ZnIn₂S₄ in the CZFN is further confirmed by the positive shifts of In3d_{3/2}/In3d_{5/2} and S2p_{1/2}/S2p_{3/2} peaks in the In3d and S2p spectra (Fig. S6b,c). The Fe2p spectra can be fitted to six peaks corresponding to Fe2p_{1/2}/Fe2p_{3/2} and satellite signals of Fe₂O₃, which move to lower binding energies and overlap with Ni Auger peaks in the case of CZFN, inferring the electron-withdrawing Fe₂O₃ during the formation of the hybrid (Fig. 2l). Conversely, in the Ni2p spectra, no obvious shift occurs on Ni2p_{1/2}/Ni2p_{3/2} and satellite peaks of Ni(OH)₂ after its coating on the surface of C@ZnIn₂S₄/Fe₂O₃ (Fig. 2m). Furthermore, when in situ irradiated XPS measurement was performed on CZFN, binding energies of C1s, Zn2p, In3d and S2p peaks under visible light irradiation positively shift by 0.07, 0.17, 0.11 and 0.11 eV, respectively, while Fe2p and Ni2p peaks undergo negative shift (by 0.21 and 0.34 eV) compared to those in the dark (Fig. 2j-m and Fig. S6b,c). Such binding energy shifts

provide vivid evidences that photoexcited electrons move to ZnIn₂S₄ and hollow C, while holes shift to Fe₂O₃ and Ni(OH)₂ during the photocatalytic process [48].

3.2. Photocatalytic performances analysis

For a more detailed investigation of the photocatalytic performance of CZFN, we synthesized a library of binary, ternary and quaternary counterparts for comparison, including C@ZnIn₂S₄ (labeled as CZ), the step iii precursor of CZFN (Fig. 3a₁); C/Fe₂O₃ (labeled as CF) and ZnIn₂S₄/Fe₂O₃ (labeled as ZF) with the deposition of Fe₂O₃ on hollow C and ZnIn₂S₄, respectively (Fig. 3a_{2,a3}); ZnIn₂S₄@Ni(OH)₂ (labeled as ZN) and Fe₂O₃@Ni(OH)₂ (labeled as FN) with the encapsulation of ZnIn₂S₄ and Fe₂O₃ into Ni(OH)₂, respectively (Fig. 3a_{4,a5}); C@ZnIn₂S₄/Fe₂O₃ (labeled as CZF), the step iv precursor of CZFN (Fig. 3a₆); C@ZnIn₂S₄@Ni(OH)₂ (labeled as CZN), C/Fe₂O₃@Ni(OH)₂ (labeled as CFN) and ZnIn₂S₄/Fe₂O₃@Ni(OH)₂ (labeled as ZFN) with the coating of CZ, CF and ZF with Ni(OH)₂, respectively (Fig. 3a_{7-a9}); and C/Fe₂O₃@ZnIn₂S₄@Ni(OH)₂ (labeled as CFZN) in reverse stacking order of ZnIn₂S₄ and Fe₂O₃ relative to CZFN (Fig. 3a₁₀). All the samples were adopted to conduct the photocatalytic reaction in the mixed vapor of CO₂ and H₂O under visible light irradiation. As shown in Fig. 3b, there is no detectable product over zero-band-gap hollow C and wide-band-gap

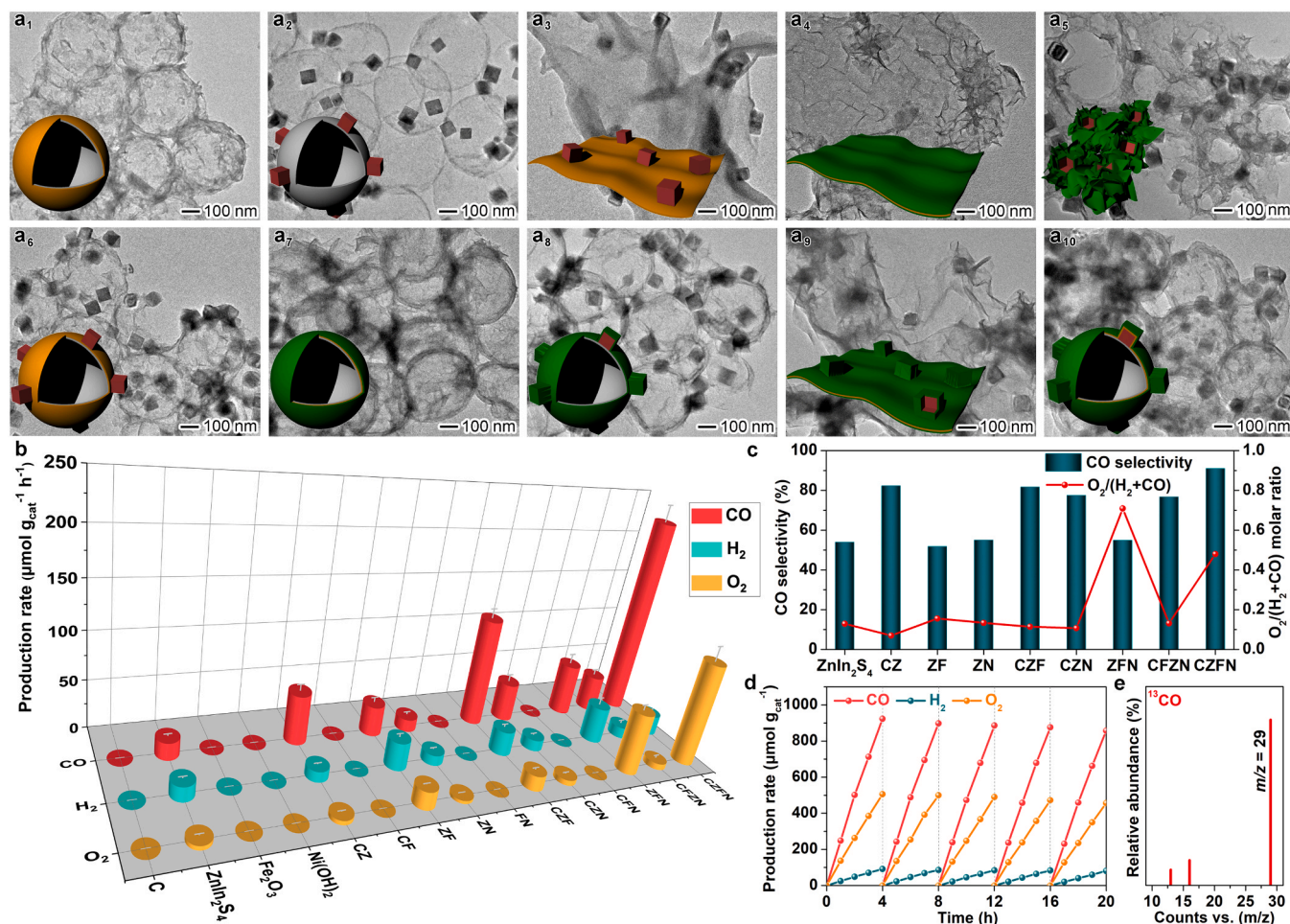


Fig. 3. Photocatalytic performance of CZFN and reference samples: (a) TEM images of binary, ternary and quaternary counterparts of CZFN: (a₁) CZ, (a₂) CF, (a₃) ZF, (a₄) ZN, (a₅) FN, (a₆) CZF, (a₇) CZN, (a₈) CFN, (a₉) ZFN, and (a₁₀) CFZN; (b) CO, H₂ and O₂ production rates under visible light irradiation in the absence of a sacrificial agent; (c) CO selectivity and molar ratio of oxidation product to reduction products; (d) recycling test of CZFN; (e) mass spectrum of ¹³CO produced over CZFN.

Ni(OH)₂ owing to the mismatching between band energy and incident light. ZnIn₂S₄ produces a trace amount of CO, H₂ and O₂, while Fe₂O₃ generates O₂ only in the presence of AgNO₃ electron scavenger because of unsuitable conduction band (CB) position for CO₂ and proton reduction half reaction (Fig. S7). Further introduction of hollow C elevates the CO yield of ZnIn₂S₄ and simultaneously suppresses the side H₂ production, but cannot effectively improve the O₂ output of Fe₂O₃. In stark contrast, Ni(OH)₂ coating decreases the CO, H₂ and O₂ production of ZnIn₂S₄, but raises the O₂ evolution of Fe₂O₃ only when AgNO₃ is added (Fig. 3b and Fig. S7). Namely, pairwise collaboration occurs in CZ and FN rather than CF and ZN. Furthermore, compared with CZ and FN, CZN and CFN exhibit no obvious enhancement in CO₂ reduction and H₂O oxidation, again excluding the positive contribution of Ni(OH)₂ coverage and C supporting to the photoactivity of ZnIn₂S₄ and Fe₂O₃, respectively. Coupling of ZnIn₂S₄ and Fe₂O₃ not only improves the evolution rates of CO and H₂, but also enables the O₂ evolution in the absence of a sacrificial agent, confirming their synergistic effect in realizing overall redox reactions. Different from ZnIn₂S₄ and Fe₂O₃, the photoactivity of ZF in CO₂ reduction and H₂O oxidation can be upgraded when intergrating with either hollow C substrate or Ni(OH)₂ outer layer. Specifically, when both hollow C and Ni(OH)₂ are involved, CZFN delivers a maximal CO production rate of 230.7 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ and O₂ production rate of 121.8 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, nearly 12.7 and 11.2 times higher than that of pristine ZnIn₂S₄ and Fe₂O₃, respectively. The AQE of CZFN in CO generation is determined to be 1.98% at 420 nm.

Contrastingly, the CO and O₂ evolution rates of CFZN are remarkably inferior, even lower than those of ZF, explicitly evincing that the stacking sequence of ZnIn₂S₄ and Fe₂O₃ is critical to the photocatalytic enhancement.

The product selectivities over CZFN and control samples are compared in Fig. 3c. It can be clearly observed that carbon-containing samples exhibit apparently higher CO selectivities in reference to other samples, further verifying the pivotal role of hollow C in hindering the side proton reduction, in accordance with our previous report [35]. Specifically, CZFN achieves the highest CO selectivity of 90.9%, 1.7-fold that of blank ZnIn₂S₄. The activity and selectivity of CZFN in CO generation also transcend most of the reported ZnIn₂S₄ based photocatalysts (Table S1). Furthermore, the molar ratios of oxidation product (O₂) to reduction products (H₂ + CO) over ZnIn₂S₄ involved samples were calculated. The O₂/(H₂ + CO) ratio is close to 1:2 stoichiometric ratio of the overall redox reactions (2CO₂ → 2CO + O₂; 2H₂O → 2H₂ + O₂) in the case of CZFN, implying the well-balanced reduction and oxidation half reactions (Fig. 3c). As for other samples, the ratio is far below or above the theoretical value, suggesting the mismatched CO₂ reduction and H₂O oxidation. To evaluate the photocatalytic stability of CZFN, five repeated cycles have been conducted with no pronounced activity decay after 20 h cycling tests (Fig. 3d). Moreover, the morphology, structure and composition of the used CZFN are well maintained when compared with the fresh one, confirming its excellent durability and reusability (Fig. S8 and S9). Inversely, photoactivity of ZF suffers from a

considerable decline under the same test conditions, convincing that the combination of C supporting and Ni(OH)₂ coating protect the encapsulated semiconductor heterojunction against photocorrosion, leading to superior stability of CZFN (Fig. S10) [49]. To our surprise, when the

used CZFN after 5 cycles, which has been stored for 7 months, was re-tested for additional 15 cycles, the activity loss is also not evident during the discontinuous cyclic test, further evidencing its extremely long-term durability (Fig. S11). Besides, ¹³C isotopic labeling

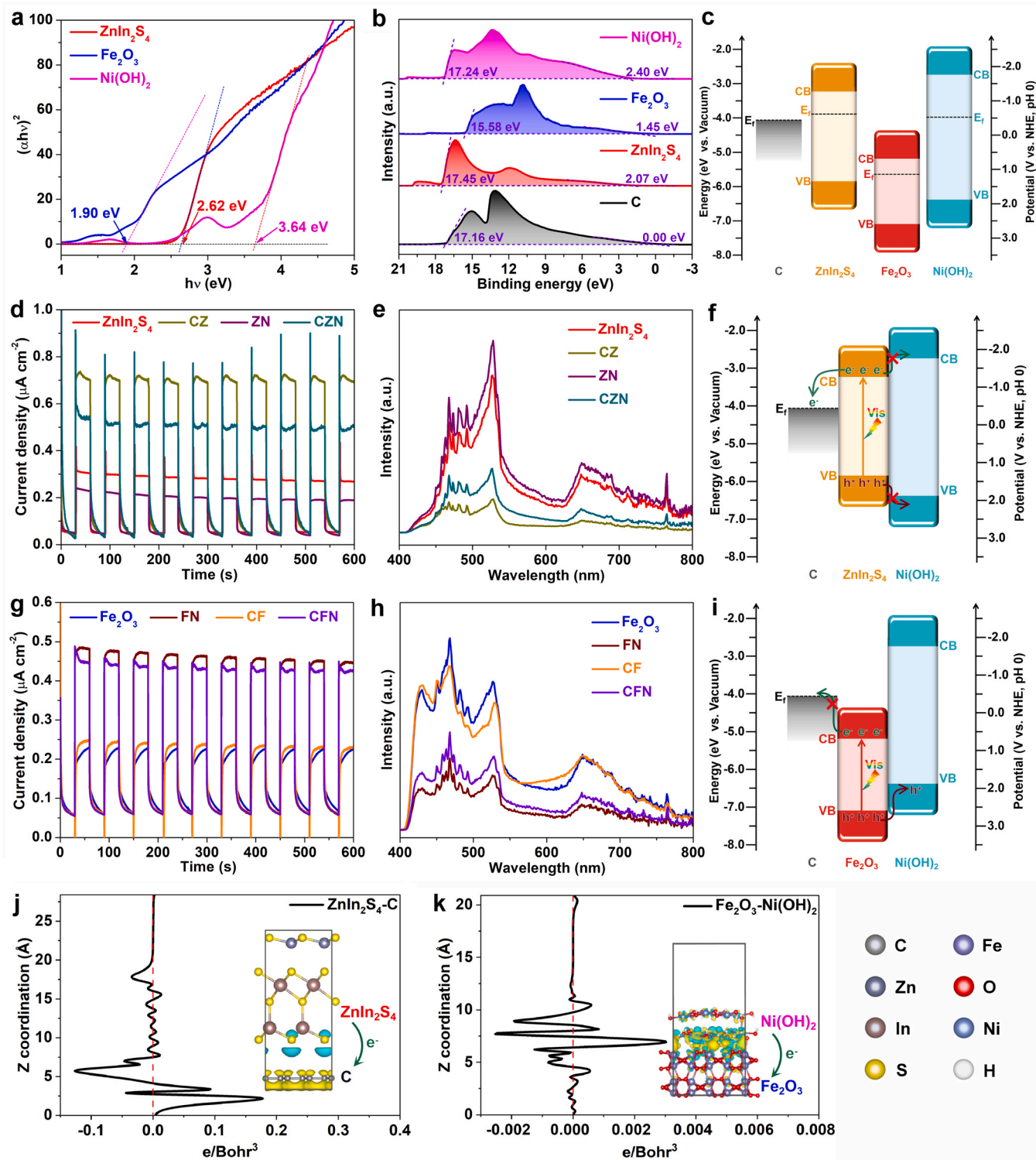


Fig. 4. Energy band alignments of the components involved in CZFN and charge transfer between them: (a) Tauc plots, (b) UPS spectra and (c) band alignments of hollow C, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂; (d) photocurrent responses and (e) PL spectra of ZnIn₂S₄-containing samples; (f) schematic illustrating the charge transfer between ZnIn₂S₄, hollow C and Ni(OH)₂; (g) photocurrent responses and (h) PL spectra of Fe₂O₃-containing samples; (i) schematic illustrating the charge transfer between Fe₂O₃, hollow C and Ni(OH)₂; (j,k) profile of the plane-averaged differential charge density along the z-axis of (j) ZnIn₂S₄-C and (k) Fe₂O₃-Ni(OH)₂ as well as their corresponding simulated differential charge density distributions at the interfaces shown in the insets (the charge accumulation region is in yellow and the charge depletion region is in blue).

experiment has been performed to track to carbon source of reduction product, in which the GC-MS signal at $m/z = 29$ strongly verifies that the generated CO indeed originates from the photoreduction of CO₂ (Fig. 3e) [50]. Stirring speed in the photocatalytic reactor has little effect on the activity and selectivity of CZFN, inferring that catalytic reaction kinetics instead of mass transfer kinetics is the decisive factor of the photocatalytic performance (Fig. S12).

3.3. Charge transfer/separation kinetics analysis

To gain an in-depth insight into the improved photocatalytic performance of CZFN, band structures of the components involved were surveyed. According to Tauc plots derived from UV-vis diffuse reflectance spectra, the E_g of ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ is estimated to be 2.62, 1.90 and 3.64 eV, respectively (Fig. 4a). Ultraviolet photoelectron spectroscopy (UPS) measurements further disclose that the work function of hollow C, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ is 4.06, 3.77, 5.64 and 3.98 eV, respectively, and the corresponding valance band maximum (VBM) is separately situated at 0.00, 2.07, 1.45 and 2.40 eV below the E_f (Fig. 4b). Namely, the E_f of hollow C, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ is located at -4.06 , -3.77 , -5.64 and -3.98 eV related to the vacuum level, which is equal to -0.44 , -0.73 , 1.14 and -0.52 V (vs. NHE, pH 0), respectively [51]. As such, the valence band maximum (VBM) of ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ is determined to be 1.34, 2.59 and 1.88 V vs. NHE, respectively. Then based on E_g , the corresponding conduction band minimum (CBM) is -1.28 , 0.69 and -1.76 V vs. NHE, respectively. According to above discussion, energy band diagrams of C, ZnIn₂S₄, Fe₂O₃ and Ni(OH)₂ are illustrated in Fig. 4c. Clearly, only narrow-band-gap ZnIn₂S₄ and Fe₂O₃ can be excited by visible light to produce photocarriers.

To evaluate the charge kinetics of the samples, we conducted photoelectrochemical and PL tests. Given the overlapped optical absorption range and approximate PL emission wavelength of ZnIn₂S₄ and Fe₂O₃, to exclude their mutual interference, transient photocurrent responses of ZnIn₂S₄-containing samples without Fe₂O₃ involved were employed to investigate the charge transfer between ZnIn₂S₄, hollow C and Ni(OH)₂. As shown in Fig. 4d, under chopped visible irradiation, compared with pristine ZnIn₂S₄, obvious enhancement in the photocurrent density is achieved by CZ, while there is a tremendous decline in the photocurrent response of ZN, evidencing that C supporter promotes charge separation in ZnIn₂S₄, while Ni(OH)₂ overlayer induces aggravated charge recombination. Moreover, CZN demonstrates a photocurrent density even lower than that of CZ, further evincing the negative contribution of Ni(OH)₂ coating to the charge separation in ZnIn₂S₄. The above statement is further confirmed by steady-state PL emission spectra (Fig. 4e), wherein the PL intensity of ZnIn₂S₄ decreases in the order: ZN > ZnIn₂S₄ > CZN > CZ, in line with the photocurrent enhancements. As illustrated in Fig. 4f, considering that the CB and valence band (VB) of ZnIn₂S₄ are respectively lower and higher than those of Ni(OH)₂, Ni(OH)₂ can neither accept electrons nor holes from ZnIn₂S₄ in terms of thermodynamics. As such, Ni(OH)₂ coating obstructs the diffusion of charges generated by ZnIn₂S₄, thus inducing serious carrier recombination. Alternatively, photoelectrons migrate from the CB of ZnIn₂S₄ to the E_f of hollow C driven by the energy difference between them. As for Fe₂O₃-containing samples without ZnIn₂S₄ involved, the photocurrent densities follow the sequence: Fe₂O₃ \approx CF < FN \approx CFN, demonstrating that Ni(OH)₂ instead of hollow C accelerates the charge separation in Fe₂O₃ (Fig. 4g). Such a statement is further validated by the PL results, wherein obvious PL quenching of Fe₂O₃ occurs after compounding with Ni(OH)₂, while there is no apparent decline in the PL intensities of CF and CFN when compared with Fe₂O₃ and FN, respectively (Fig. 4h). As depicted in Fig. 4i, the CBM of Fe₂O₃ is in lower position relative to the E_f of hollow C and CBM of Ni(OH)₂, making it impossible for the movement of photoelectrons from Fe₂O₃ to them. Instead, holes migrate from Fe₂O₃ to Ni(OH)₂ with higher VB position. Based on above discussion, it can be concluded that C supporter and Ni(OH)₂ outer layer selectively trap

photoelectrons and holes from ZnIn₂S₄ and Fe₂O₃, respectively. Furthermore, electronic coupling between them and charge transfer direction at the interfaces were further reflected by DFT calculation. As visualized in Fig. 4j and k, intensive plane-averaged differential charge densities (DCDs) $\Delta\rho$ oscillation along z direction highlights a noticeable charge redistribution at ZnIn₂S₄-C and Fe₂O₃-Ni(OH)₂ interfaces, and the corresponding differential charge density distributions manifest the ZnIn₂S₄-to-C and Ni(OH)₂-to-Fe₂O₃ electron transfer, reaffirming the interfacial charge transfer direction between them [52].

In terms of the samples with both ZnIn₂S₄ and Fe₂O₃ involved, ZF exhibits a significantly enhanced photocurrent density compared with the components involved, corroborating efficiently charge transfer between them (Fig. 5a). In light of the staggered band alignment between ZnIn₂S₄ and Fe₂O₃, there are two possible mechanisms for the transfer and separation of photogenerated carriers in ZF: traditional Type-II and direct Z-scheme models. According to 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) EPR spectra, under visible light irradiation, bare ZnIn₂S₄ only generates DMPO- $\bullet\text{O}_2^-$ signal since its VBM is not positive enough to oxidize H₂O/-OH to $\bullet\text{OH}$, while Fe₂O₃ only produces DMPO- $\bullet\text{OH}$ signal since its CBM is not negative enough to reduce O₂ to $\bullet\text{O}_2^-$ (Fig. 5b,c). In stark contrast, both DMPO- $\bullet\text{O}_2^-$ and DMPO- $\bullet\text{OH}$ signals are generated by ZF, and the signal intensities are obviously strengthened in comparison with those of ZnIn₂S₄ and Fe₂O₃. These results rule out the possibility of the formation of conventional Type-II heterojunction with the reason that neither signals attributing to DMPO- $\bullet\text{O}_2^-$ nor DMPO- $\bullet\text{OH}$ would be detected when photoelectrons transfer to the CB of Fe₂O₃ along with the diffusion of holes in the opposite direction (Fig. 5d) [53]. Therefore, the charge transfer should follow the second scenario. That is the photoelectrons in the CB of Fe₂O₃ recombine with holes in the VB of ZnIn₂S₄, leaving holes in the VB of Fe₂O₃ and electrons in the CB of ZnIn₂S₄ with stronger redox capabilities for $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ generation, respectively (Fig. 5d). Based on aforementioned discussion, an S-scheme charge transfer mechanism is proposed (Fig. 5e). Given that ZnIn₂S₄ possesses higher E_f relative to Fe₂O₃, upon their contact, to minimize their E_f difference, free electrons flow from ZnIn₂S₄ to Fe₂O₃, giving rising to electron-deficient ZnIn₂S₄ and electron-rich Fe₂O₃, in accordance with XPS results [54]. Consequently, an internal electric field (IEF) pointing from ZnIn₂S₄ to Fe₂O₃ creates at the interface together with the upward and downward band bending of ZnIn₂S₄ and Fe₂O₃, respectively. Upon visible irradiation, ZnIn₂S₄ and Fe₂O₃ are excited to produce photoelectrons and holes. Under the combined effect of IEF and bent bands, weak CB electrons of Fe₂O₃ transmit across the interface and recombine with the VB holes of ZnIn₂S₄. Meanwhile, strong ZnIn₂S₄ electrons and Fe₂O₃ holes are preserved for CO₂ reduction and H₂O oxidation, respectively.

Compared with ZF, CZF and ZFN exhibit further increased photocurrent response, suggesting that both hollow C supporting and Ni(OH)₂ coating accelerate the charge separation in ZF (Fig. 5f). When hollow C and Ni(OH)₂ are simultaneously involved, CZFN delivers the highest photocurrent density, reflecting their synergy in maximizing the charge separation efficiency. By contrast, CFZN exhibits an inferior photocurrent as benchmarked against ZF, in consistence with the photocatalytic results. As depicted by electrochemical impedance spectroscopy (EIS) (Fig. 5g), the arc of Nyquist plot reduces in the order: CFZN > ZF > ZFN > CZF > CZFN, meaning the lowest interfacial charge-transfer resistance in CZFN. As expected, the average electron lifetimes (τ_n) of CZFN is obviously longer when compared with its counterparts (Fig. 5h), which was investigated by open-circuit voltage decay (OCVD) in the dark (Fig. S13), supporting that more efficient charge separation and transfer exerts a pronounced effect on the prolonged τ_n . Taking the architectures of the samples into consideration, electron migration from ZnIn₂S₄ to C supporter is facilitated by the large-area C-ZnIn₂S₄ interface in CZF, while hole transportation from Fe₂O₃ core to Ni(OH)₂ shell is smoothed by the their full contact in ZFN. For CZFN, the ZnIn₂S₄ \rightarrow C electron flow and Fe₂O₃ \rightarrow Ni(OH)₂ hole movement occurs in parallel, contributing to well-balanced charge transport. As for CFZN, though

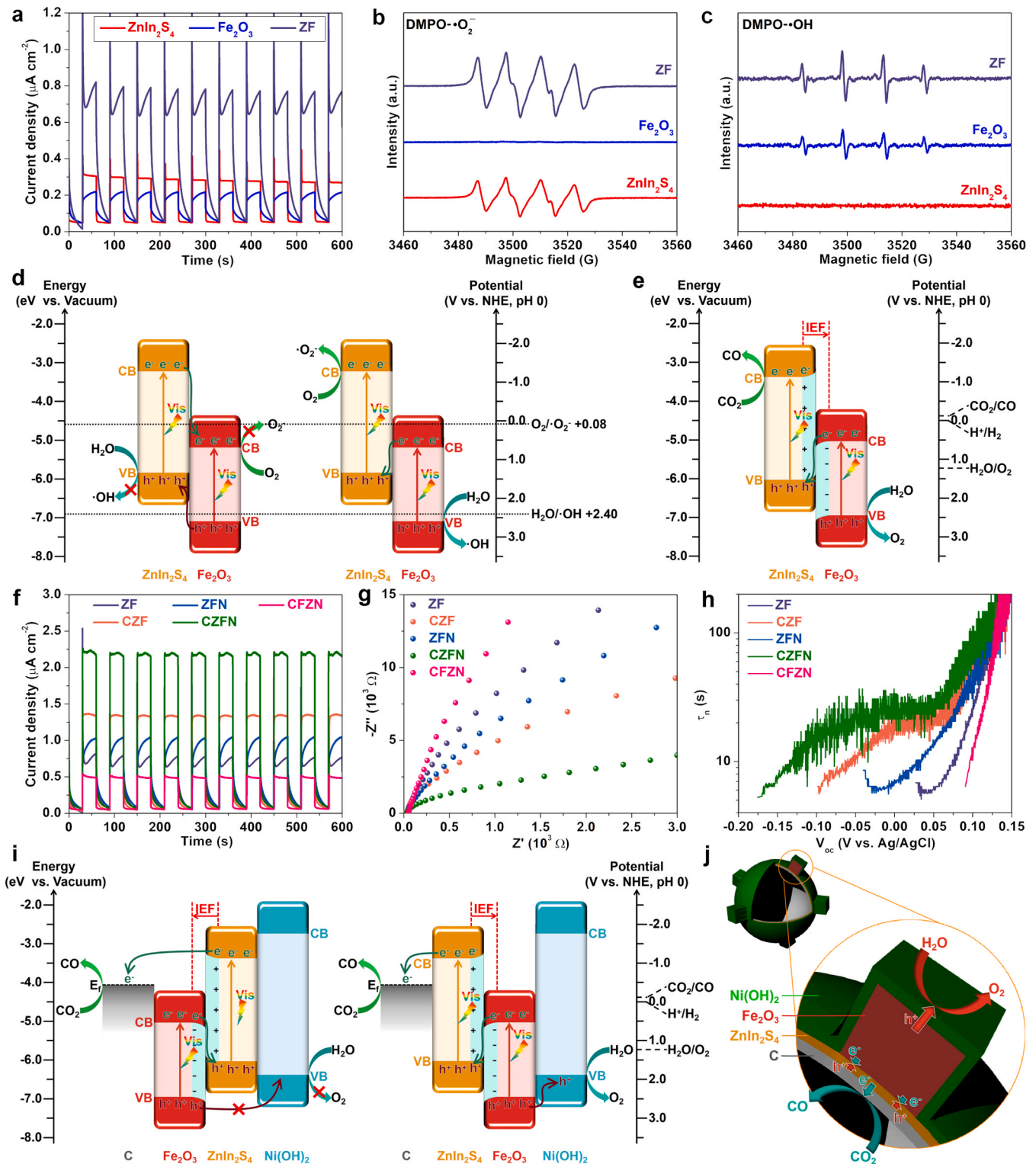


Fig. 5. Charge separation/transfer kinetics analysis of CZFN and reference samples: (a) photocurrent responses, (b) DMPO- $\cdot\text{O}_2^-$ and (c) DMPO- $\cdot\text{OH}$ EPR spectra of ZnIn_2S_4 , Fe_2O_3 and ZF; (d) Type-II and direct Z-scheme charge transfer pathways between ZnIn_2S_4 and Fe_2O_3 ; (e) proposed S-scheme charge transfer mechanism of ZF; (f) photocurrent responses, (g) EIS Nyquist plots, and (h) average electron lifetimes of CZFN and reference samples; (i,j) energy band diagrams and photocatalytic reaction mechanisms of CFZN and CZFN.

photoelectrons migration from ZnIn_2S_4 to C substrate is enabled by the interfacial contact between them, hole transmission from Fe_2O_3 to Ni(OH)_2 outer layer is blocked by ZnIn_2S_4 interlayer. The sluggish diffusion out of holes inevitably causes unbalanced carrier utilization and serious charge recombination (Fig. 5i). Based on above analysis results,

the reaction mechanism of CZFN is illustrated in Fig. 5i and j. Under illumination, weak Fe_2O_3 electrons drift across the Fe_2O_3 - ZnIn_2S_4 interface and recombine with powerless ZnIn_2S_4 holes. Concurrently, strong ZnIn_2S_4 electrons diffuse to inner hollow C for CO_2 reduction, and powerful Fe_2O_3 holes transmit to outer Ni(OH)_2 for H_2O oxidation. The

inward and outward migration of photocreated electrons and holes in opposite directions matches well with results of in-situ irradiated XPS, accounting for thorough charge separation and thus the highest photoactivity of CZFN.

3.4. Surface reaction dynamics analysis

Apart from charge separation/transfer kinetics, surface reaction dynamics were further explored to unravel the origin of photocatalytic enhancements. Fig. 6a shows the linear sweep voltammetry (LSV) curves for O_2 evolution conducted in KOH electrolyte, in which ZFN and CZFN display lower onset potentials and higher current densities in reference to ZF and CZF, manifesting that $\text{Ni}(\text{OH})_2$ coverage enriches the reaction sites for H_2O oxidation [55]. When LSV curves are collected in Ar and CO_2 -saturated KHCO_3 electrolyte, the higher current density in CO_2 atmosphere relative to that in Ar atmosphere can be attributed to the cathodic current generated by CO_2 reduction (Fig. 6b) [56]. Compared to ZF and ZFN, CZF and CZFN exhibit larger CO_2 reduction current densities, affirming that C substrate offers highly active centres for CO_2 fixation [57]. Fig. 6c presents the CO_2 adsorption isotherms of CZFN and its components at 298 K. Obviously, in line with the BET data, CZFN

displays a CO_2 adsorption capacity higher than those of ZnIn_2S_4 , Fe_2O_3 and $\text{Ni}(\text{OH})_2$, but lower than that of hollow C, further validating that C supporter is the decisive component adsorbing CO_2 molecules, mainly owing to its porous nature and large specific surface area.

To in-depth understand the reaction pathway and underlying reasons of the increased reactivity in CO_2 photoreduction, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out for precisely tracking the reactive intermediates during the CO_2 reduction on the surface of ZFN and CZFN. As shown in Fig. 6d and e, for both samples, there is no obvious DRIFTS signal in the dark. Irradiated by visible light, obvious adsorption bands can be recorded by ZFN, including bidentate carbonate (b-CO_3^{2-} : 1651, 1575 and 1557 cm^{-1}), monodentate carbonate (m-CO_3^{2-} : 1635, 1472, 1456 and 1292 cm^{-1}), bicarbonate (HCO_3^- : 1433, 1417, 1395 cm^{-1}), carboxylate ($\text{CO}_2^{\bullet-}$: 1682, 1668 and 1248 cm^{-1}), and the intensities of which gradually increase with the elongation of irradiation time [58–60]. Especially, carboxyl (*COOH) signal is detected at 1540, 1521, 1506 and 1145 cm^{-1} , which is regarded as the key intermediate during the CO_2 -to- CO reduction. As for CZFN, the intensities of absorption bands assigned to *COOH , b-CO_3^{2-} , m-CO_3^{2-} , HCO_3^- and $\text{CO}_2^{\bullet-}$ increase more dramatically under the same irradiation time when compared with ZFN. Additionally, a new

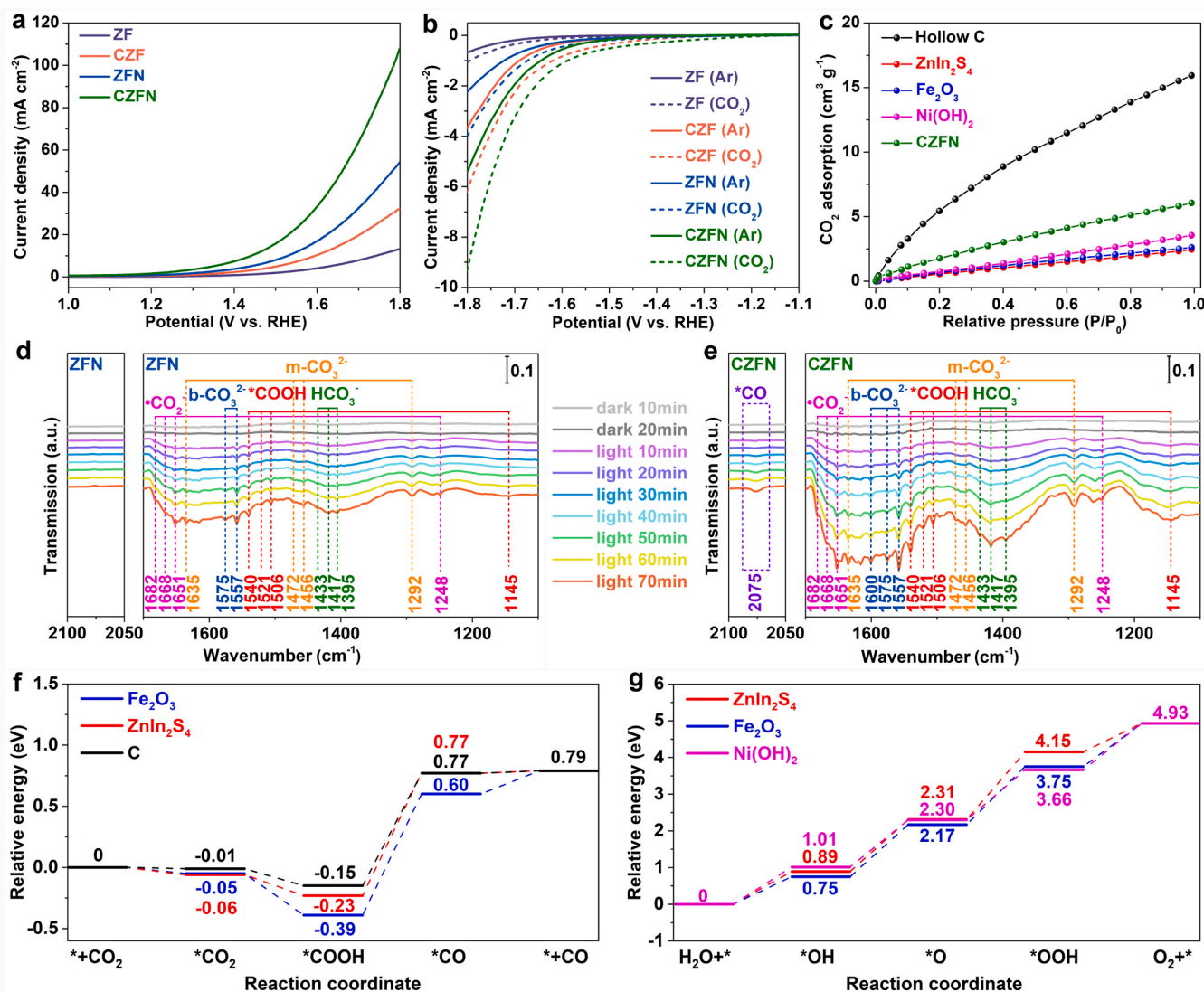


Fig. 6. Surface reaction dynamics analysis of CZFN and reference samples: (a,b) LSV curves for (a) CO_2 reduction and (b) O_2 evolution; (c) CO_2 adsorption isotherms; (d) in situ DRIFT spectra of CO_2 reduction with H_2O over (d) ZFN and (e) CZFN; (f) free energy diagrams of CO_2 -to- CO reduction on ZnIn_2S_4 , Fe_2O_3 and hollow C; (g) free energy diagrams of H_2O -to- O_2 oxidation on ZnIn_2S_4 , Fe_2O_3 and $\text{Ni}(\text{OH})_2$.

band appearing at 2075 cm^{-1} is indicated for the formation of $^*\text{CO}$, which is consistent with its superior activity in CO formation [61]. Based on the DRIFTS results, the plausible CO_2 reduction pathway is $\text{CO}_2 \rightarrow ^*\text{CO}_2 \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow \text{CO}$, which is more favorable when C substrate is introduced into ZFN.

To further gain insight into the CO_2 photoreduction mechanism on CZFN, DFT calculations were performed to reveal the pivotal role of hollow C in achieving both the high activity and selectivity in CO production. Fig. 6f (also Fig. S14a) shows the free energy diagrams for CO_2 -to-CO reduction on ZnIn_2S_4 , Fe_2O_3 and hollow C, as well as the optimized configurations of the intermediates adsorbed on the surface. For all the models, the key step for CO production is the coupling of $^*\text{COOH}$ with a proton/electron pair to generate $^*\text{CO}$. Clearly, in the case of hollow C, the free-energy change (ΔG) value for this step is 0.92 eV, smaller than those of ZnIn_2S_4 (1.00 eV) and Fe_2O_3 (0.99 eV), demonstrating that C supporter lowers the energy barrier for CO formation. We also compare the Gibbs free energy changes during the H_2O oxidation to O_2 on ZnIn_2S_4 , Fe_2O_3 and $\text{Ni}(\text{OH})_2$ surface. As displayed in Fig. 6g (also Fig. S14b), OOH^* formation is the endergonic rate-limiting step, and the free energy barrier ΔG_{OOH^*} for $\text{Ni}(\text{OH})_2$ (1.36 eV) is lower than those of ZnIn_2S_4 (1.84 eV) and Fe_2O_3 (1.58 eV). Hence, the presence of $\text{Ni}(\text{OH})_2$ overlayer is more beneficial for H_2O oxidation in term of lower energy barrier. Based on above experimental and theoretical results, it is very comprehensive to conclude that the inner C and outer $\text{Ni}(\text{OH})_2$ layers of CZFN separately co-catalyze the CO_2 reduction and H_2O oxidation in a more favorable way.

4. Conclusion

In summary, a hollow multi-shelled nanoreactor with S-scheme heterojunction sandwiched between spatially separated layered double-cocatalysts is constructed via the step-by-step deposition of ZnIn_2S_4 , Fe_2O_3 and $\text{Ni}(\text{OH})_2$ on hollow carbon spheres. In the smart design, IEF and band bending in the inserted $\text{ZnIn}_2\text{S}_4/\text{Fe}_2\text{O}_3$ S-scheme heterojunction promote the recombination of carriers with lower redox abilities, and separate powerful photoelectrons and holes in ZnIn_2S_4 and Fe_2O_3 , which move to the inner carbon supporter and outer $\text{Ni}(\text{OH})_2$ overlayer for CO_2 reduction and H_2O oxidation inside and outside the chamber, respectively. Comprehensive experimental and theoretical investigation reveals that the large-area contact and strong electronic coupling between the components smoothen the interfacial charge transfer and boost the electron-hole separation. Meanwhile, C substrates and $\text{Ni}(\text{OH})_2$ outer layers afford highly active sites for CO_2 reduction and H_2O oxidation, reduce the rate-determining barrier for CO formation and O_2 evolution, and suppress the occurrence of side proton reduction and undesirable photocorrosion on the semiconductor surface. Benefiting from the simultaneous optimization of charge kinetics and surface reactivity, the quaternary nanoreactor not only delivers a benchmarked activity ($230.7\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$) and selectivity (90.9%) for CO production, markedly superior to a series of counterparts, but also realizes the stoichiometric production of reduction and oxidation products. The results obtained in this study provide a general and unique strategy to balance the separation, transfer and consumption of electrons and holes for overall redox reactions, and inspire the developments of two-dimensional earth-abundant wrapping cocatalysts for artificial photosynthesis.

CCRediT authorship contribution statement

Kingwei Zhang: Conceptualization, Investigation, Data curation, Writing – original draft. **Yili Song:** Software, Calculus analysis, Validation. **Xiangyue Niu:** Conceptualization, Investigation. **Xinyuan Lin:** Investigation, Data curation. **Shuxian Zhong:** Investigation. **Hongjun Lin:** Resources. **Botao Teng:** Methodology, Validation, Funding acquisition. **Song Bai:** Conceptualization, Formal analysis, Supervision, Writing – review & editing, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123445.

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